WASTE TO CLEAN SYNGAS: AVOIDING TAR PROBLEMS

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Abstract

Syngas from gasification of carbon-rich feedstock is used for power generation as well as for the production of synthetic fuels and commodity chemicals. Tar removal forms a major challenge in the effort to make these syngas valorisation technologies technically and commercially feasible. Tar removal methods can be divided into two categories: (1) primary methods or treatments inside the gasifier, and (2) secondary methods or hot gas cleaning after the gasifier. The most important features of the primary and secondary tar removal methods, as well as the most recent developments in this field, are reviewed and discussed in this paper. For advanced syngas applications (e.g. gas engines), primary measures are generally not sufficient. In that case, primary methods can be used as a tool to optimise the gas composition for the secondary cleaning step. Corona plasma for tar removal is discussed in more detail. This promising technology will be used in future research on the cracking of real tars obtained from refuse derived fuel (RDF) pyrolysis.

Introduction

Waste-to-Energy (WtE) technologies are emerging as promising routes for reducing the fossil fuel dependency of the world's energy supply. Gasification systems are regarded as an efficient way to transform organic fuels, some of them classified as renewable (i.e. biomass and waste) into high value products. Raw product gas generated from gasification contains impurities (particulate matter, tars, sulphur compounds, etc.) that must be abated to meet process requirements and emission standards. The level of cleaning required depends greatly on the syngas end-use application, ranging from heat or power applications to the production of synthetic fuels. A broad range of techniques is developed to reduce or remove the contaminants in raw product gas, some techniques focus on a single contaminant while others are able to remove multiple contaminants simultaneously. This paper reviews the technologies for removing tars (i.e. condensable hydrocarbons) from raw product gas. This gas cleaning step is often designated as the Achilles heel of the process[1] and a key issue in the commercialisation of gasification processes for high-end applications (i.e. syngas fired fuel cells).

The terminology that is being used to refer to product gas from gasification processes is not always consistent. The term 'syngas' (or synthesis gas) is widely used as an industry shorthand to refer to this gaseous product stream. However, technically, syngas is a gas stream composed of only H_2 and CO derived from a steam and oxygen gasification process[2]. Even though the term syngas is not entirely accurate, both terms (syngas and product gas) will be used interchangeably in order to blend in with the current practices in the industry and published literature.

Gasification

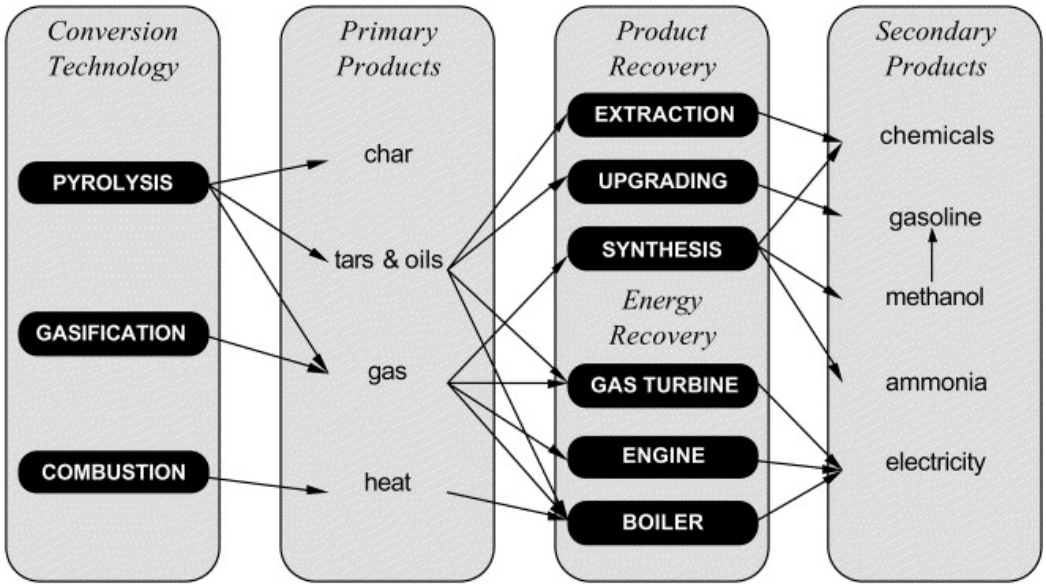

Figure 1: Thermochemical biomass conversion: products and applications.[3]

Incineration (or combustion), gasification and pyrolysis are the main thermochemical conversion technologies available for the thermal treatment of solid fuels (e.g. biomass, waste). As shown in Figure 1, these processes yield different products that require the appropriate treatment for energy and/or material recovery. Gasification is generally defined as the thermochemical conversion of a solid or liquid carbon-based feedstock into a combustible gaseous product by the supply of a gasification agent. Air, oxygen, steam, carbon dioxide, or a combination of these, are the most commonly used gasification agents. Air blown gasifiers typically achieve temperatures up to 900 °C-1100 °C, while oxygen blown gasifiers can reach temperatures up to 1000 °C-1400 °C. High temperature heterogeneous reactions quickly convert the feedstock into a combustible gas containing CO, CO_2, H_2, H_2O, CH_4, trace amounts of higher hydrocarbons, inert gases originating from the gasification agent and various contaminants such as small char particles, ash and tars.[4] Direct gasification processes utilise an oxidising gasification agent to partially oxidise the feedstock. The oxidation reactions supply the necessary energy to maintain the required process temperature. Indirect gasification processes, on the

other hand, require an external energy source. Steam is a popular non oxidising gasification agent as it is relatively cheap, easy to come by, and increases the hydrogen content of the syngas.[5]

Gasifiers

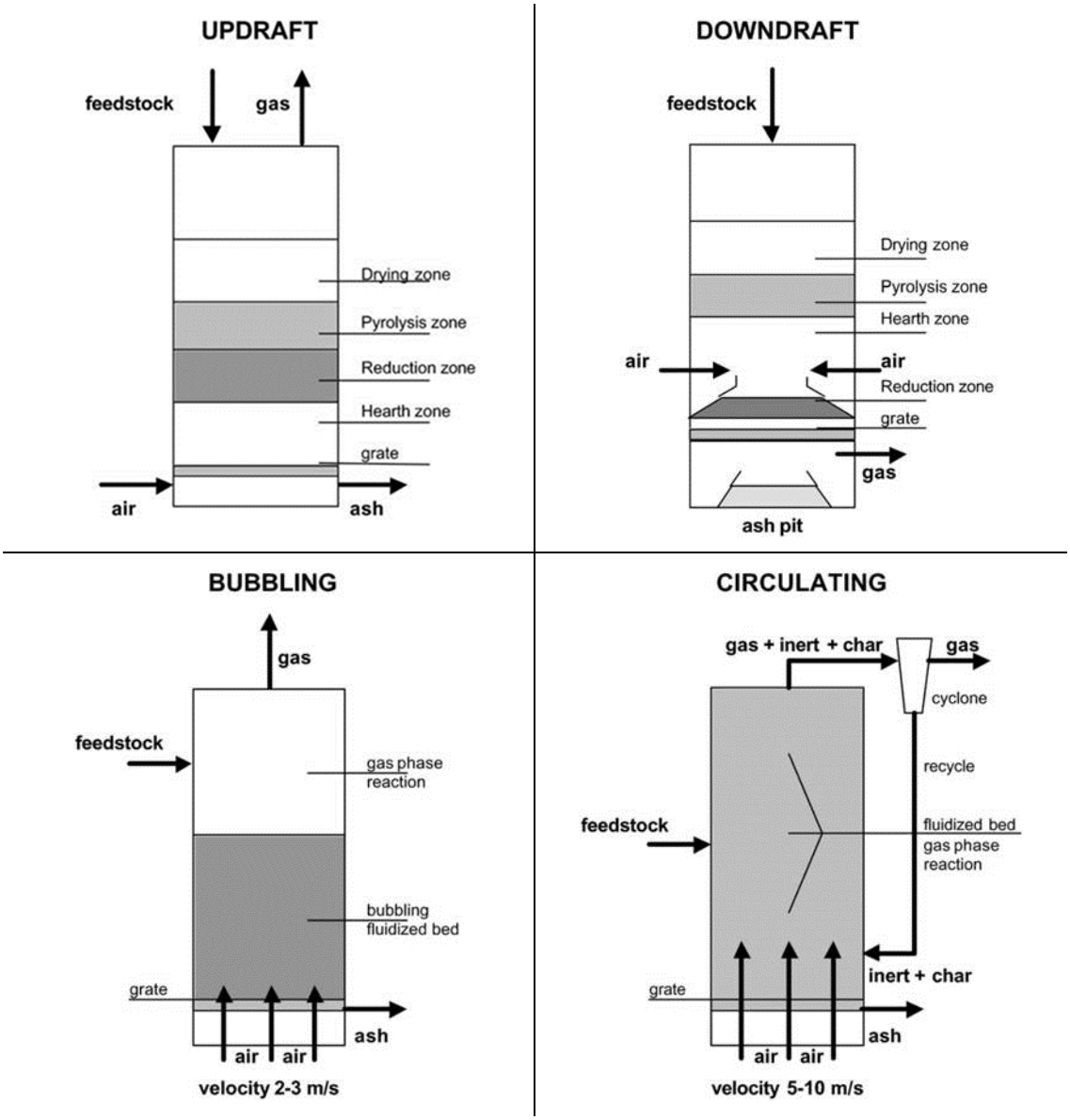

Figure 2: Gasifier configurations.[5]

The most frequently used gasification reactors encountered in practice are fixed bed (updraft or downdraft) and fluidised bed (bubbling or circulating) reactors. Figure 2 shows the working principle of these gasifier configurations. In an *updraft* reactor, the feed material is added from the top while the gasification agent is introduced from the bottom of the reactor (counter-current). Updraft gasifiers typically produce

a gas with a high tar content, up to 10% (100 g Nm^{-3}). The tars formed in the pyrolysis zone are carried upward by the flowing hot gas stream, hereby escaping partial oxidation. In the *downdraft* (co-current) configuration, the feedstock is supplied from the top while gas is introduced at the sides above the grate. The raw product gas is withdrawn below the grate. All products pass through a high temperature reaction zone at the base of the reactor, which explains why the tar level in downdraft gasifiers tends to stay below 0.1% (1 g Nm^{-3}). The main shortcoming is the less efficient internal heat exchange compared to the updraft gasifier. In *fluidised bed* gasifiers, the fixed bed of fine solids (typically silica-sand) expands through the action of the upward flowing oxidising agent. The fixed bed is isothermal and the velocity of the gas sent through the bed controls the degree of bed expansion. Low velocities (below 3 m/s) result in a bubbling fluidised bed with only a small degree of expansion to ensure bed material and char stay inside the reactor. High gas velocities (5-10 m/s) cause the bed to expand throughout the entire reactor volume which results in a significant entrainment of solid particles from the reactor. This problem is tackled by positioning a cyclone directly downstream of the reactor to capture and recycle the solids fraction. The product gas of fluidised bed reactors contains intermediate tar levels (~10 g Nm^{-3}). The level of tars in the product gas is of course not solely determined by the gasifier design. Equally important are the feedstock composition and processing conditions, especially the type of oxidant/bed material used, the temperature-time history of the gas and particles, the point of feed introduction, the feed particle size distribution; to name a few.[2,6]

In the last decades, a wide range of gasification technologies have been developed to treat different types of feedstock (e.g. biomass, refuse derived fuel, sewage sludge). Gasification processes are known to be relatively sensitive to variations of input and process conditions. Strict process monitoring and control are mandatory in order to ensure high conversion efficiencies and limited formation of unwanted by-products (especially tars). The feed material should be homogeneous in terms of physical (e.g. particle size) as well as chemical properties (e.g. heating value). Hence, waste streams generally require pretreatment in the form of shredding, screening, sorting, drying and/or pelletisation. The terms *solid recovered fuel* (SRF) and *refuse derived fuel* (RDF) are used to describe solid waste that has been processed this way. In the literature, these terms are often used interchangeably but this is not entirely correct. Recently, the European Standardization Committee finalised the SRF European Standards (EN15359).[7] Imposing a quality standardisation is expected to stimulate and facilitate the trading of fuels among producers and users. SRF is a high quality alternative to fossil fuel produced from commercial waste including paper, cardboard, wood, textiles and plastics. It can be produced to a range of specifications to meet customer requirements.[8] RDF is produced from household waste which includes biodegradable material as well as plastics. RDF usually has a lower calorific

value than SRF.[8] On-going research and improved insights into how the gasification process works, have led to the development of specialised gasification reactors. High-temperature slagging gasifiers, for example, are capable of recovering both the energy and material content of the products. Operating at temperatures above the ash fusion temperature (1000 °C-1500 °C) results in a nonleachable, vitrified slag with a higher quality compared to the vitrified bottom ash fraction found in conventional gasification.[9] Plasma melting technologies were initially developed to treat hazardous waste streams such as printed circuit boards (PCBs) and asbestos.[10] The high temperatures that can be reached through plasma torches (~5000 °C) ensure a complete destruction of toxic contaminants. More recently, these processes have also been optimised for energy valorisation and fuel production. Plasma gasification is often combined with vitrification for the treatment of solid wastes containing high fractions of organics. Potentially useful applications of the high quality vitrified slag that is obtained, are discussed elsewhere in this issue.[11] Both single-stage and two-stage plasma gasification systems exist. The waste is treated directly with plasma jets in single-stage gasifiers. In the two-stage configuration, gasification is followed by plasma cleaning of the raw syngas.[12] This design overcomes a number of drawbacks inherent to the system combining gasification and plasma conversion in a single reactor (i.e. relatively low throughput, poor control of volatile organic compounds (VOCs) and tars, and a low conversion efficiency to a valuable syngas). Other types of gasification technologies have been tried and are being developed, for a variety of waste streams. More detailed process descriptions and applications can be found in the literature.[4,13,14]

Tar in biomass gasification

Regardless of the research effort dedicated to improving gasification systems and the gas cleaning step in particular, there exist few biomass-fired gasifiers that have proven to be a commercial success – besides the gasification systems that directly (co-)fire the product gas into boilers. The more advanced (and efficient) ways to valorise syngas call for more stringent gas specifications. Tars in particular have proven to be very problematic. It remains a challenge to develop a feasible way to strongly reduce tar levels in syngas without compromising the gas quality. Tar tolerance levels for gas engines, gas turbines and fuel cells equal 50, 5 and 1 mg Nm^{-3}, respectively.[15,16] Although some uncertainty exists regarding these values, mainly due to a lack of data on long-term operations, they are assumed to be reliable estimates.

Tar classification

The most widely accepted definition of tars states that tars are all organic compounds with a molecular weight higher than benzene. Over the years, this definition has been refined in different ways. ECN[6] has developed a very comprehensive classification with a focus on the tar properties and typical components, see Table 1.

Table 1: Tar classification.[6]

Class 1	***GC undetectable tars:*** This class includes the heaviest tars that condense at high temperatures even at very low concentrations.	gravimetric tars
Class 2	***Heterocyclic components:*** These are components that generally exhibit high water solubility, due to their polarity.	pyridine, phenol, cresol, quinoline
Class 3	***Aromatic components:*** Light hydrocarbons that are not important in condensation, however might cause issues concerning their solubility in water.	xylene, styrene, toluene
Class 4	***Light polyaromatic hydrocarbons (2-3 rings PAH's):*** These components condense at relatively high concentrations and intermediate temperatures.	naphthalene, methyl-naphthalene, biphenyl, ethenylnaphtalene, acenaphtylene, acenaphtene, fluorene, phenanthrene, anthracene
Class 5	***Heavy polyaromatic hydrocarbons (4-5 rings PAH's):*** These components condense at relatively high temperatures at low concentrations.	fluoranthene, pyrene, benzo-anthracene, chrysene, benzo-fluoranthene, benzo-pyrene, perylene, indeno-pyrene, dibenzo-anthracene, benzo-perylene

The total tar concentration is not the most important parameter, it is the tar dew point which defines the point at which tars start to be problematic. The tar dew point is defined as the temperature at which the total partial pressure of tar equals the saturation pressure of tar.[6] At this point, tar condensation can occur, if not hindered by slow kinetics. Typical tar dew points are between 150 °C and 350 °C, which is usually far above the lowest process temperature (~30 °C). Needless to say tars will condense and cause severe problems if their level is not strongly reduced before the product gas reaches these low temperatures. Tars in classes 1, 4 and 5 exert a strong influence on the tar dew point: they readily condense even at high temperature and can cause major fouling problems and efficiency loss. Class 2 and 3 tars (e.g. phenol, naphthalene) exert a limited influence on the tar dew point but they are water soluble, which means they create pollution problems in the aqueous phase of

downstream wet gas cleaning equipment. Naphthalene is known to crystallise at the inlet of gas engines.

Tar reduction methods

A lot of research effort has been and is still put into developing an effective and economically feasible method for tar reduction, a challenging task. The available methods can be divided into two main categories depending on the location where tar is removed. Primary methods directly abate tar inside the gasifier; secondary methods act outside the gasifier (i.e. hot gas cleaning). The different options available within these two treatment types are discussed in more detail in the following subsections. This paper intends to provide an overview of the most important findings reported in the literature, instead of giving a detailed technology review. The references indicated in the text will lead the reader to more detailed information.

Primary methods. In biomass gasification, the operating parameters play a key role in the product distribution, including tar generation. The important parameters include temperature, equivalence ratio (ER), type of feed, pressure, gasifying medium, residence time, etc. Clearly, these parameter settings also depend on the type of gasifier used.[17] The optimisation of both the gasifier configuration and its operating conditions, referred to as *self-modification*, plays an important role in tar abatement. The ultimate primary treatment method(s) would eliminate the need for secondary treatment steps. However, such a scenario is still far away from real life experience.

The gasification temperature is an operating parameter that strongly influences the product distribution, especially the tar level. High operating temperatures (at least 750 °C) are required to reach high carbon conversion of the feedstock and low tar content in the resulting product gas. However, at gasification temperatures exceeding 850 °C there is a rapid increase in the formation of 3- and 4-ring aromatics (class 4 and 5) together with other unwanted by-products. Figure 3 summarises the research performed on different feed materials for which the optimal temperature range with regard to a number of critical process performance indicators is determined.[18] Apart from the tar content, these indicators include the gas heating value, the char conversion and the risk of sintering.

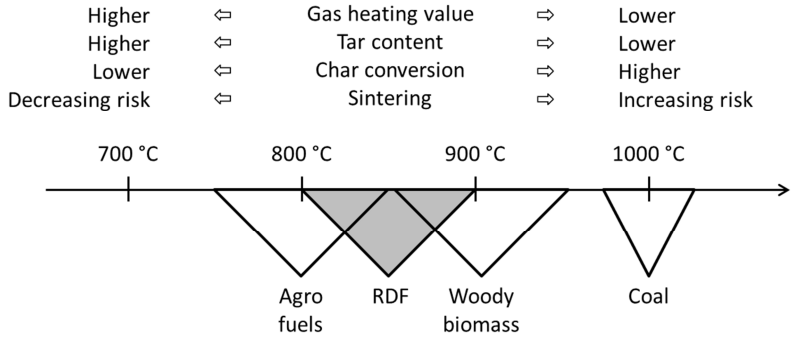

Figure 3: Typical gasification temperatures for various feedstock and influence of temperature change on critical process characteristics.[18]

The ER also exerts a strong influence on the type and quantity of tars produced. As the ER increases, tar concentration decreases as there is more oxygen available to react with the volatiles in the flaming pyrolysis zone.[18] At higher gasification temperatures, this effect of ER becomes more important. But again, the ER cannot be chosen too high as this would lead to decreased H_2 and CO concentrations and increased CO_2 concentration in the syngas, hereby causing the gas heating value to drop.

Devi and co-workers[18] give a comprehensive overview of the influence of different gasifying media on product gas composition and heating value, as well as on tar composition and concentration. It is mentioned that using steam as gasification agent (on its own or in combination with other gases) can speed up tar cracking, with results from other studies confirming this.[19] Carefully selecting the proper steam to biomass ratio ensures there is no need to compromise on gas quality.

A different type of primary tar reduction measure is the use of bed additives or catalysts. There exist numerous studies that discuss the selection of the most appropriate additives/catalysts for tar abatement.[2,6,16,20,21] The 'ideal' catalyst material is cost-effective, and combines a high efficiency with a high selectivity towards tars (as opposed to high quality syngas components). Among the catalytically active bed materials, dolomite and limestone are well known. These rock materials can reach tar conversions of up to 95%, they are cheap and are considered to be disposable, which explains their popularity. Most important disadvantages are the heterogeneous nature of these materials as well as the fact that they are soft, which results in high attrition rates combined with carryover of solids from the bed. Olivine is found to have a higher attrition resistance than dolomite and a comparable catalytic activity. Alternative catalytically active minerals have been described and tested by a number of researchers, detailed information can be found in the literature.[2,6,16,20,22]

Apart from the naturally occurring minerals, there exists a wide range of metallic and metallic oxide synthetic catalysts that have been applied for in-bed tar conversion. Nickel-based catalysts are the most popular. As coke formation and attrition proved to be major problems, the conventional Ni-catalysts were made more robust by combining them with (earth)alkali oxides as in the Ni/alumina catalyst.

It was already mentioned earlier that the gasifier design affects the tar yield. Hence, more advanced gasifier designs – variations of some kind on the basic configurations – have been developed and tested. The most popular concept is the two-stage gasifier where the pyrolysis zone is separated from the reduction zone. Tars formed during the first stage (pyrolysis) are cracked in the second stage (reduction). The Asian Institute of Technology (AIT), Thailand, studied a two-stage gasifier with two levels of air intakes. They report a significantly lower tar production (40 times less) compared to a single-stage gasifier operating under similar conditions.[23] Researchers at the Technical University of Denmark designed a two-stage gasifier combining pyrolysis of the feed with subsequent partial oxidation of the volatiles inside a charcoal bed.[24] Hofbauer and his team[25] developed a new fluidised bed gasification technique, a two-stage gasifier with a fast internally circulating fluidised bed (FICFB). The fluidised bed gasifier is divided into two zones, a gasification zone with steam as the fluidising medium and a combustion zone with air. Between these two zones, a circulation of bed material is created which acts as heat carrier from the combustion (exothermic) to the gasification (endothermic) zone. The total tar amount could be reduced to 1 mg Nm^{-3}, and to even lower values with the addition of catalyst to the bed material. The Belgium-based company Xylowatt[26] developed the NOTAR® gasification reactor, a co-current multistage gasification technology with a physical separation between the three phases of the gasification process (i.e. pyrolysis, combustion and reduction). In the pyrolysis zone, heat is used to break down the biomass feed into charcoal (fixed carbon) and into pyrolysis gas at temperatures between 200 °C and 700 °C. In the combustion zone, the pyrolysis gas is oxidised at very high temperatures (1200 °C) with a controlled intake of air, hereby cracking the tars produced in the pyrolysis zone. In addition to breaking down the products of the pyrolysis process, the oxygen allows CO_2 and H_2O to be produced. In the reduction zone, the CO_2 and H_2O are reduced by the activated charcoal to produce a syngas primarily composed of H_2 and CO. Finally, a gas conditioning unit lowers the total tar and dust concentration to below 10 mg Nm^{-3}. There are several projects running, mainly focused on small scale biomass CHP (Combined Heat and Power) applications, but also on industrial syngas applications.

In practice, there is a reluctance to implement these improved designs on a commercial level, despite the fact that several attempts have proven to be effective

in tar reduction. This lack of enthusiasm is linked to the complex gasifier constructions and/or the decreased gas heating value due to the partial oxidation.[27]

Based on the reported literature, it is clear there is still a lot of work to be performed in order to get a better understanding of how these primary tar reduction measures influence the entire gasification process. For a number of process parameters (e.g. temperature, ER) there exists a trade-off between tar reduction efficiency and syngas quality. At the same time, these conditions affect the performance of catalytically active bed materials, which in turn suffer from several drawbacks such as a possibly negative impact on product gas quality, catalyst deactivation and carry-over of fines. Table 2 summarises the most important techno-economic implications of implementing a selected number of primary tar reduction methods.[28]

Table 2: Main techno-economic implications of applying primary tar measures, adapted from Kiel et al.[28]

Benefits / cost savings	**Disadvantages / extra costs**
Higher gasification temperature (>850 °C)	
Less water-soluble tars	Agglomeration risk
Higher output temperature from gasifier	More condensable tars (3- and 4-ring aromatics)
Lower C-content of ashes	+ increased tendency for aerosol and condensate
Less water treatment requirements	formation
	Increased internal energy use
	Lower net power output
Dolomite addition	
Only few water soluble tars	Dolomite storage, dosing equipment
Less condensable tars	Quality requirements and costs of dolomite
Less contaminants in product gas	addition
Decreased aerosol and condensate formation	Increased ash production
Lower C-content of ashes	Quality and saleability of the ashes
Less water treatment requirements	Extra CO_2 emission
Longer residence time in gasifier	
Less water-soluble tars	Effect on gasifier dimensions
Lower C-content of ashes	More condensable tars + increased tendency for
Less water treatment requirements	aerosol and condensate formation

Secondary methods. Secondary tar reduction methods consist of hot gas cleanup downstream of the gasifier. They can be divided into physical (or mechanical) and chemical methods. There is a wide variety of physical methods available: cyclones, filters (baffle, fabric or ceramic), rotating particle separators, electrostatic precipitators, and scrubbers (water or organic-liquid based). Many of these physical systems require lower temperatures in order to operate effectively. This is easily explained by the fact that tars start to condense at temperatures below ~450 °C, and form aerosols within the gas stream. These aerosols are heavier than the vapours and can be removed by physical forces, similar to particulate matter removal. The main issues are the reduced overall system efficiency (in case partial gas cooling is

required), as well as the creation of an extra waste stream (especially in wet systems) that requires treatment. These physical tar reduction methods are in general well understood, a number of elaborate reports are available in the literature.[2,16,29]

Chemical methods are further subdivided into thermal cracking, catalytic cracking and plasma cracking methods. Often these treatments take place in a secondary reactor. They aim at complete tar conversion, in contrast to physical techniques that usually generate a residual waste stream. If chemical equilibrium would be attained inside the gasifier, tars would not be present, even at moderate temperatures. Unfortunately, real life experience proves otherwise. The different cracking methods attempt to more closely approach chemical equilibrium by increasing reaction rates of tar decomposition.[2]

Thermal cracking of tars involves the conversion of tars into lighter gases by subjecting the tars to a sufficiently high temperature for a certain time. Typically, temperatures between 1100 °C and 1300 °C are employed; the lower the temperature, the higher the residence time required for effective cracking. For example, naphthalene is reduced by more than 80% in about 1 s at 1150 °C, while obtaining a similar reduction at 1075 °C can take more than 5 s.[15,30]

The section on primary methods already discussed the influence of temperature on the tar level of the product gas. The focus here is on cracking downstream of the gasifier. The most effective way to thermally crack tars is through partial oxidation by adding oxygen or air to the product gas.[31] Obviously, the product gas components are also partially oxidised, which leads to a decrease in heating value and possible complications when using the gas in conventional gas turbines or engines.[6] It has been reported that thermal cracking downstream of a gasifier could also increase soot production, which implies an increased particulate load on cleanup or processing equipment.[2]

Catalytic cracking is used in both primary and secondary tar reduction methods. The former employ catalysts for in-bed tar conversion, while the latter convert tars downstream of the gasifier in a separate reactor. Catalysts reduce the activation energy for tar decomposition, which explains why catalytic cracking takes place at lower temperatures than thermal cracking. On the positive side, the use of catalysts avoids some of the costs associated with higher temperature operation. But on the negative side, catalysts increase the complexity of the process, along with other operational challenges related to reduced catalyst activity (i.e. poisoning, fragmentation, or carbon deposition).[2] Sutton and co-workers[21] summarised the criteria for catalysts as follows: (1) the catalysts must be effective in removing tar; (2) if the desired product is pure syngas (H_2 and CO), the catalysts must be capable of

reforming methane; (3) the catalysts should provide a suitable H_2/CO ratio for the intended process; (4) the catalysts should be resistant to deactivation as a result of carbon fouling and sintering; (5) the catalysts should be easily regenerated; (6) the catalysts should be strong; and (7) the catalysts should be inexpensive.

As with in-bed materials, natural minerals as well as metallic and metal oxide synthetic catalysts can be used for tar conversion in downstream reactors. An extensive range of catalysts has been developed for use in catalytic beds and monoliths. These catalysts are classified into groups, the number and names often differ in the literature. Anis et al.[22] give a detailed description of the following six groups: nickel-based catalyst, non-nickel metal catalysts, alkali metal catalysts, basic catalysts, acid catalysts, and activated carbon catalysts. Similarly, Han and Kim[17] classify catalysts into four groups (nickel-based, alkali metal, dolomite, and novel metal catalysts). Yung et al.[32] follow a slightly different approach in their review of catalyst compositions and their influence on activity for product gas conditioning. The catalyst is divided into three primary components: (1) an active catalytic phase or metal; (2) a promoter, to increases activity and/or stability; and (3) a high surface area support that facilitates dispersion of the active phase. These excellent reviews provide in depth information about the different catalyst materials available for tar reforming.

Plasma cracking of tars is a relative newcomer among the different reforming methods. Plasma is known as the fourth state of matter. It contains free radicals, ions and excited molecules that create a highly reactive atmosphere.[12] These reactive species carry enough energy to initiate tar decomposition reactions.[33] Plasmas are classified as thermal or non-thermal, based on the relative temperatures of the electrons, ions and neutrals. Thermal plasmas are in thermal equilibrium, with the bulk gas species and electrons at the same temperature. In contrast, non-thermal plasmas have the ions and neutrals at a much lower temperature, whereas the electron temperature is significantly higher.

Thermal plasmas are applied in single-stage and two-stage plasma gasification systems. In single-stage systems, the plasma (generated by an electric arc) mainly serves as heat source which means the process temperature can be controlled independently from fluctuations in feed quality and supply of gasifying agent.[12] In addition, thermal tar cracking takes place in this high temperature environment. In two-stage systems, the plasma refines the raw syngas upon exiting the gasification reactor. Plasco Energy Group completed a two-stage plasma-arc waste demonstration plant in Ottawa (Canada) to process 85 tonnes per day of municipal solid waste.[34] Plasma torches, installed in an oxygen-starved conversion reactor, interact with the gas phase only, hereby limiting electricity demand. Tetronics

developed a similar process (the Gasplasma® process) which combines fluidised bed gasification with plasma cleaning of the resulting syngas.[35] The plasma conversion reactor provides the high-temperature environment for converting residual tars and chars, in combination with vitrification of the ash into a non-leaching slag.

Non-thermal plasma systems are successfully applied in pollution control, mainly for the removal of VOCs.[36,37] Several types of non-thermal plasma systems are available, including pulsed corona, dielectric barrier discharges, DC corona discharges, radiofrequency (RF) plasma, and microwave plasma. ECN has performed research on gliding arc plasmas. This type of plasma lies somewhere in between thermal and non-thermal plasma: 20% of the energy is dissipated in the thermal part, 80% in the 'cold' part.[6] The results were not very promising, as the tar conversion observed during their tests reached only 40%. The energy level of the electrons was found to be too low, resulting in a limited radical production and thus a low functionality for tar removal. Furthermore, the gliding arc reactor did not show any selectivity towards specific hydrocarbons, not even at elevated temperatures. Hence they are all equally converted. Among the non-thermal plasmas, pulsed corona plasma is believed to be the most promising technique.[2] At the Technical University of Eindhoven (TUe, the Netherlands), research has been performed on the removal of tar model compounds in synthetic gas mixtures, at different temperatures. Experimental results have indicated complete conversion of naphthalene by pulsed plasma processing at moderate temperatures (~400 °C).[38] This technology will be discussed in more detail in a following section.
These more advanced plasma processes for tar cracking still need to mature. Commercial scale development is hindered by the limited lifetime of certain plasma sources (also: pulsed power devices), their high costs, and high energy demand of the overall process (electricity as energy source).

Tar decomposition

Tar decomposition mainly occurs due to cracking, steam and dry reforming reactions, as shown below[39]:

Cracking: $pC_nH_x \rightarrow qC_mH_y + rH_2$

Steam reforming: $C_nH_x + nH_2O \rightarrow (n + x/2)H_2 + nCO$

Dry reforming: $C_nH_x + nCO_2 \rightarrow (x/2)H_2 + 2nCO$

Carbon formation: $C_nH_x \rightarrow nC + (x/2)H_2$

where C_nH_x represents tar and C_mH_y represents hydrocarbons with smaller carbon number than C_nH_x.

Jess[40] investigated the conversion of tars in the presence of hydrogen and steam, using naphthalene, benzene and toluene as model compounds. Experiments were performed at temperatures of 700-1400 °C, residence times of 0.2-3 s and different gas phase concentrations of hydrogen, steam and tars. The order of reactivity of the different model compounds was found to be: toluene >> naphthalene > benzene. Jess' experimental observations lead to an overall reaction scheme of tar decomposition in the presence of H_2 and H_2O, shown in Figure 4. The results indicate that benzene is a key component in tar decomposition. High temperatures (at least 1400 °C) are required to convert all the cracking products (soot or solid carbon, and lighter hydrocarbons) into the desired syngas components (i.e. H_2 and CO).

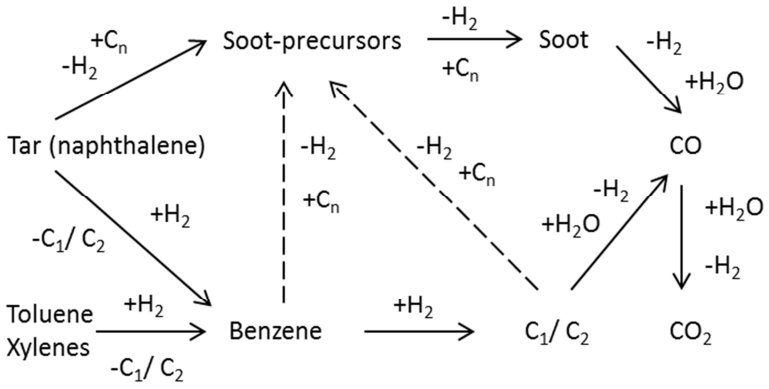

Figure 4: Simplified reaction scheme of tar conversion in the presence of hydrogen and steam (C_1, C_2, C_n represent hydrocarbons with *1*, *2*, *n* carbon atoms).[40]

There exist several studies that investigate both the catalytic and noncatalytic tar model compound decomposition. Devi and co-authors[39] give an elaborate overview of the available literature in this research domain.

It is generally assumed that radical reactions play a vital role in tar cracking, both in an inert atmosphere and in a gasification atmosphere (i.e. CO_2, H_2O, H_2).[19,41] The main reaction steps are: (1) radical-forming reactions caused by the breaking of chemical bonds, (2) propagation reactions through the formation of new chemical bonds, (3) hydrogen transfer, (4) isomerisation reactions, and (5) termination reactions in which two radicals react with each other.[19] The type of products formed (second reaction step) is determined by the gas phase composition. Vreugdenhil and Zwart[19] list the possible scenarios:

- In an inert environment the tar radicals may decompose, but they may also react with other tars to form larger tar molecules and ultimately soot. Thus, radical formation does not directly result in tar decomposition but initially in even worse (larger) tar molecules.

- In a H_2O or CO_2 environment there is a chance of the radical reacting with H_2O or CO_2, contributing to tar decomposition and increasing the rate at which it takes place.
- In a H_2 environment the radical can react with H_2 fairly readily, causing a tar molecule to be reformed. In this way, H_2 inhibits the tar decomposition rate.
- In an $H_2/H_2O/CO_2$ atmosphere the reaction rate of the tar radicals with H_2 is higher than the reaction rate with H_2O or CO_2. Tar decomposition as a result of the tar radicals reacting with H_2O and/or CO_2 is therefore suppressed by the presence of H_2.

Looking into the available literature, it is clear there has been continuous interest in tar related issues, starting from coal conversion studies in the 1980s.[42] Surprisingly, almost all studies are performed on the decomposition of tar model compounds or pyrolysis tars (coal or biomass) instead of focusing on tars from (biomass) gasification plants. Even though interest in advanced syngas applications (e.g. fuel cells, Fischer-Tropsch) has been booming for over more than a decade, this did not boost research on tar cracking in biomass gasification.

Corona plasma for tar removal

Nair et al.[38] investigated pulsed corona plasma as an alternative technique to thermal or catalytic methods for tar removal. Pulsed high voltages are applied to the corona plasma reactor, resulting in the generation of reactive species that initiate the tar cracking reactions. The majority of the experiments have been performed on naphthalene. Some experiments focused on other tar model compounds (i.e. toluene, phenol and phenanthrene). In addition, proof of concept studies were done on a wood fired gasifier. These tests, carried out at 200 °C, aimed at demonstrating the feasibility of combined tar and dust removal by corona discharges. Overall, the corona system proved to be robust in the challenging operating conditions. Nevertheless, the researchers concluded the system was not mature enough for industrial applications. The energy use was too high and the system should preferably operate at higher temperatures, closer to the gasifier exit temperature. Thus, lab scale experiments on tar model compounds and different operating temperatures were carried out to gain a better understanding of the chemical mechanisms and the system performance at higher temperatures.

Detailed descriptions of the lab setups used for the experimental work can be found elsewhere.[38] Matching the pulse power source with the reactor is a critical point in the system design. Proper matching results in a high energy transfer efficiency from the pulse source to the reactor, Nair[38] reports values of 90% at 400 °C. With naphthalene as a model compound, experiments are carried out in different gas

compositions and at different temperatures. Since there is great interest to get a better understanding of tar decomposition in raw syngas from biomass gasification, synthetic fuel gas mixtures (N_2 + CO + CO_2 + H_2) are used in the experiments. The primary mechanism for tar removal was identified to be oxidation through O radicals, initiated by CO_2 dissociation.[38] Hydrogen acts as the main terminating component for the oxygen radicals, other studies confirm this result.[19]

The energy efficiency of plasma processes is often debated and is the main reason why these technologies are still struggling to become commercially feasible. Nair et al.[38] found that energy use for naphthalene removal decreased with increasing temperature (up to 500 °C). Both from the kinetic model and the experimental results, the optimum temperature for tar removal was concluded to be around 400 °C, with an energy use of 200-250 J L^{-1}. Figure 5 shows the naphthalene removal at 400 °C in various gas mixtures, as a function of the energy supplied to the gas phase. When comparing the gas mixtures with and without H_2, it is observed that hydrogen has a strong inhibiting effect on naphthalene removal.

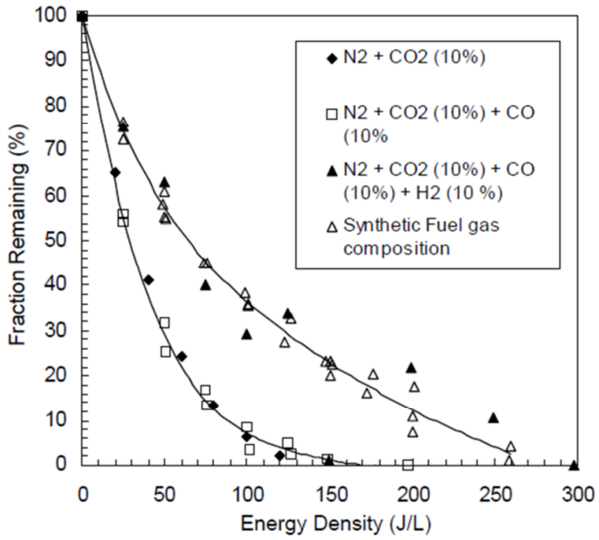

Figure 5: Naphthalene removal (3-5 g Nm^{-3}) at 400 °C in various gas mixtures, as a function of the gas phase energy density (J L^{-1}).[38]

The research performed by Nair and his colleagues is certainly a step in the right direction. The decomposition of tar model compounds was investigated in gas mixtures that closely resemble syngas produced from gasification of carbon-rich feedstock. The authors of this paper intend to take this research a step further. The experimental plan consists of (1) performing experiments at higher temperatures (up to 1200 °C), (2) investigating the decomposition behaviour of both tar model compounds (namely naphthalene) and real tars generated from RDF pyrolysis experiments, (3) carrying out sensitivity analyses for the most important process

parameters (i.e. process temperature, plasma energy input, tar initial concentration, gas composition).

The first part of the experimental plan would give an idea of the feasibility of implementing a plasma cracking reactor directly at the exit of the gasifier. Furthermore, the authors would like to investigate if a synergetic effect exists between thermal tar cracking and plasma tar cracking. In other words, the experiments intend to mimic the conditions found in a secondary tar cracking unit where *thermal plasma* (vs. non-thermal plasma) tar cracking takes place. This type of tar cracking system is explained in more detail in the section *Secondary methods*.

The second part of the experimental work would lead to a better understanding of the behaviour of real tars compared to tar model compounds. There is a lack of data on this topic, despite the fact that, for more than a decade, both the industry and other researchers have shown great interest to learn more about it. The last part of the experimental plan would result in a more fundamental insight into the relationships between the input and output variables of the process which in turn can lead to an improved, more robust system design.

Conclusions

There are still not many gasifiers operating commercially on biomass or waste feed. The ones that do, usually fire the product gas directly into boilers. More advanced ways to valorise syngas include electricity production using gas engines, gas turbines or fuel cells, and the production of synthetic fuels. These high-end applications call for more stringent gas requirements. Tars in particular can cause major system failures due to blockages and fouling of process equipment. The main challenge is to develop a gas cleaning system that strongly reduces tar levels without compromising on the syngas quality.

Tar removal methods can be divided into two categories: the primary methods that act inside the gasifier, and the secondary methods that are implemented downstream of the gasifier. Primary methods include the optimisation of the gasifier configuration and its operating conditions (i.e. *self-modification*), as well as the use of active bed materials or catalysts. Obviously, the type of feedstock and the gasifier configuration have a strong influence on the product gas properties. Other important process parameters are the gasifier temperature, the equivalence ratio (ER) and the type of gasifying medium. It might seem straightforward to implement these primary tar removal methods, but practical observations prove otherwise. For many process parameters, a trade-off exists between tar removal efficiency and syngas quality. Furthermore, the catalyst material added to the bed can have a negative impact on

the gas heating value, in addition to the problems related to catalyst deactivation and the carryover of fines.

There have been many attempts to develop gasifier systems that produce syngas with low tar levels. The two-stage gasifier, with the pyrolysis zone separated from the reduction zone, is the most popular design. Although these types of gasifiers have proven to be effective, they are not yet implemented on a commercial level. The main concerns are the complex reactor constructions as well as the decreased gas heating value caused by the partial oxidation taking place.

The implementation of primary tar removal methods alone, is not adequate to meet the high quality standards imposed by advanced syngas application technologies. Thus, primary methods are combined with secondary methods – also referred to as hot gas cleaning methods – that are categorised into physical and chemical systems. The physical systems are well understood as they have already been used for many years in gas cleaning. The main disadvantages are the fact that they create an extra waste stream (particularly in wet systems), and can cause a reduction in the overall system efficiency because gas cooling is often required prior to cleaning.

Chemical methods are subdivided into thermal cracking, catalytic cracking and plasma cracking methods. These treatments generally take place in a secondary reactor and aim at complete tar conversion. Thermal cracking requires high temperatures (around 1200 °C) that are usually attained by adding small amounts of oxygen or air to the product gas. Of course, this approach compromises the syngas quality. Catalytic cracking methods offer the advantage of operating at lower temperatures, hereby avoiding particular costs associated with high temperature operation. The downside is that the use of catalysts increases the complexity of the process. The process performance needs to be closely monitored as reduced catalyst activity can cause severe operational issues. Plasma tar cracking is a relatively new method. Thermal plasma methods operate at high temperatures, while non-thermal plasmas are also effective at moderate temperatures. The plasma cracking methods are still in a development phase. However, there are some successful applications reported in the literature. Corona plasma tar cracking has been studied at the Technical University of Eindhoven, mainly on tar model compounds in synthetic gas mixtures. The results are promising and the authors of this paper will extend this research by applying corona plasma to real tars (obtained from RDF pyrolysis) at higher operating temperatures. The goal is to obtain a better insight into the system behaviour when it is operating close to gasification conditions encountered in practice. At present, plasma systems still lack robustness and commercial viability. Therefore, the industry calls for more representative testing facilities. The possibility to perform long-term test runs on pilot scale installations would generate valuable

process knowledge that could improve plasma system design. As a first step, plasma systems need to demonstrate their robustness and high waste-to-energy conversion efficiency on a smaller scale. This would stimulate the construction of large scale systems, with lower operating costs compared to pilot scale installations.

In Enhanced Landfill Mining (ELFM), the aim is to valorise the landfill material through maximising the recycling of materials, and to convert the energy potential of the recycling residues into sustainable electricity and heat. Part of the recycling residues (processed into RDF or SRF) can be converted into syngas. Evidently, excavated waste treatment suffers from similar problems as fresh waste treatment. Tars are a key issue in the development of advanced WtE technologies and effective syngas cleaning technologies.

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